Co-operative project “PEFC durability” of the Canadian National Research Council (NRC) and the German Helmholtz Geselschaft (HGF)

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Introduction

The life-time of polymer electrolyte fuel cells (PEFC) is one of the crucial factors for commercialization in high volume markets. Consequently, the research on degradation processes and phenomena and the improvement of life-time is an important area. A German-Canadian collaboration is funded by the Helmholtz Foundation (Germany) and the National Research Council of Canada. The project is focussed on establishing the relationships between the MEA microstructure and fuel cell performance, identifying the primary causes of the major failure modes, the corresponding degradation mechanisms and degradation rates and providing the fundamental understanding of the influence of the operating conditions on the degradation of the MEA on spatial resolved level.

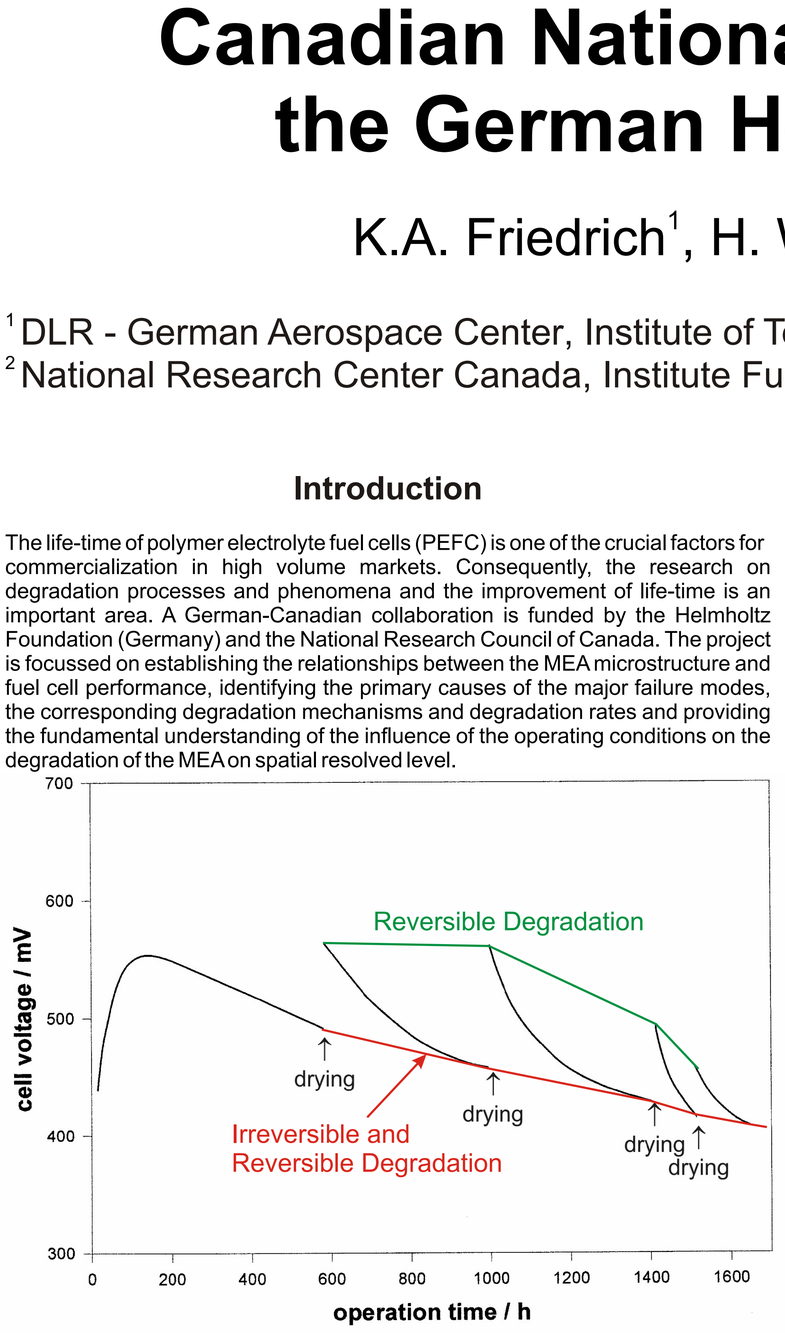

Fig. 1: Cell voltage as function of time at constant loading

Experimental Methods

For this purpose at the DLR spatial resolved measurements will be performed with in-situ and ex-situ methods. Current density measurements with a printed circuit board (PCB) as a bipolar plate will be performed in order to investigate the local operating conditions and performance.

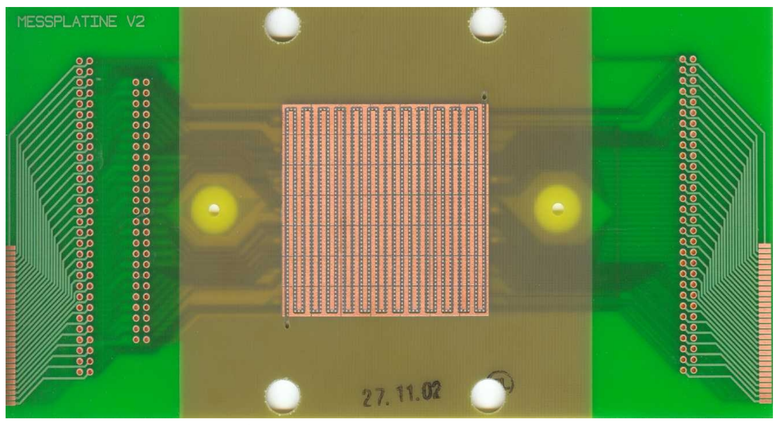

Fig. 1: Printed curcuit board for current density measurements

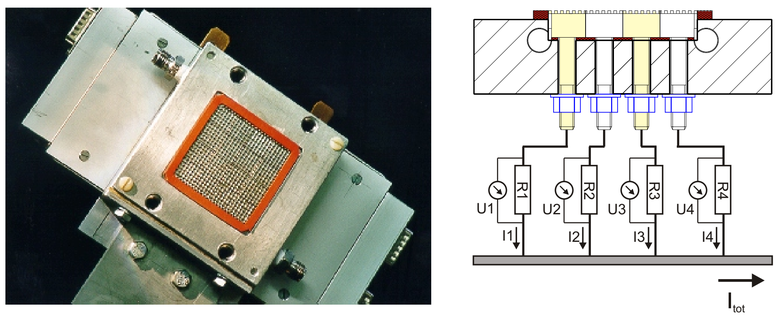

Fig. 2: Left photograph of the old version for current density measurements, which will be used for the measurement at preset current distribution; right: scheme of the measurement arangement

In addition to current density measurements the cells will be in-situ investigated by electrochemical impedance spectroscopy (EIS), which allows to separate the effect of the degradation process for each electrode and to quantify the effect on the fuel cell performance for each electrode.

The main problem of all electrochemical in-situ methods is that the evaluation of the measurement data can only be performed in the limits of the used model, whereas information from other methods are needed to verify or to support the model. For this purpose the fuel cell components will be analyzed with various methods after operation, which allows to detect and to identify the different degradation processes. At DLR, for the physical analysis of the degradation processes scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDX) , X-ray photoelectron spectroscopy (XPS), porosimetry (mercury intrusion and nitrogen adsorption), temperatur programmed desorption, oxidation and reduction and other methods are used to analyze the structure and the surface composition of the electrodes and their components. The in-situ and ex-situ investigations will be complemented by modeling activities.

Physical Characterization

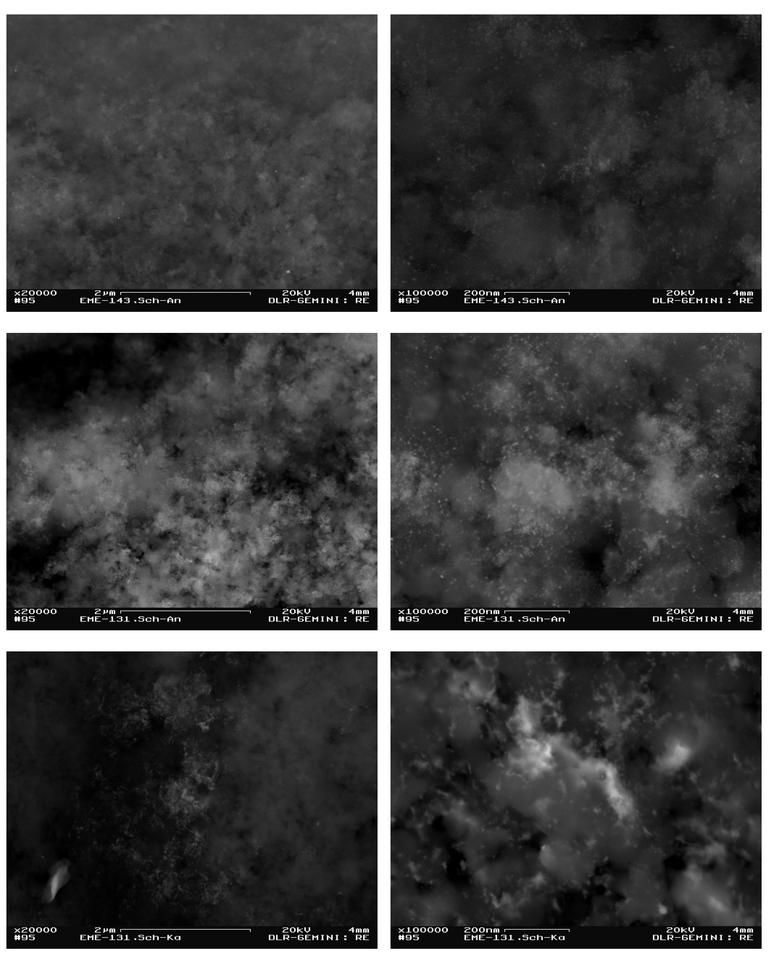

Fig. 3: SEM images of a new electrode (on top), an used anode (middle) and an used cathode (bottom) with 20000 fold (left) and 100000 fold (right) magnification

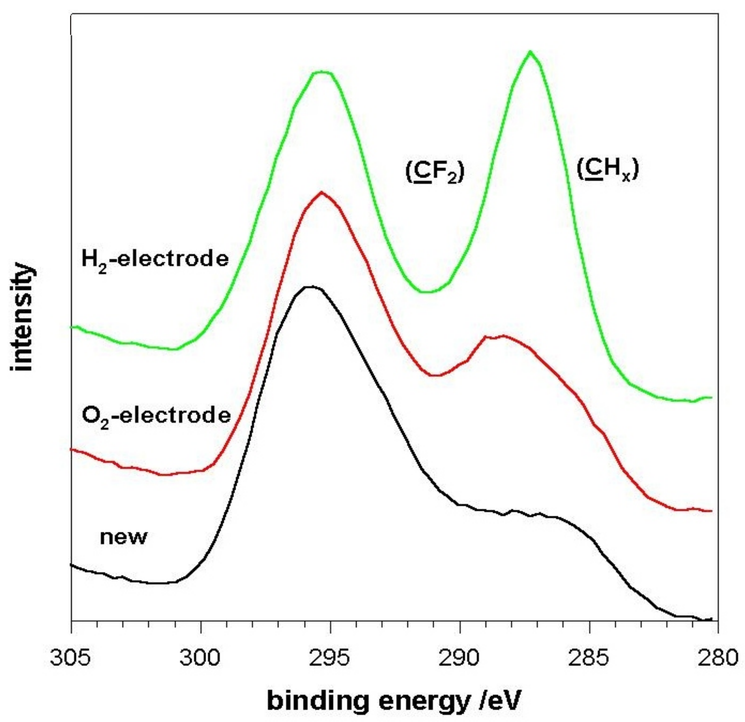

Fig. 4: X-ray photoelectron spectra of used and new electrodes (E-Tek); green: used anode, red: used cathode, black: new electrode

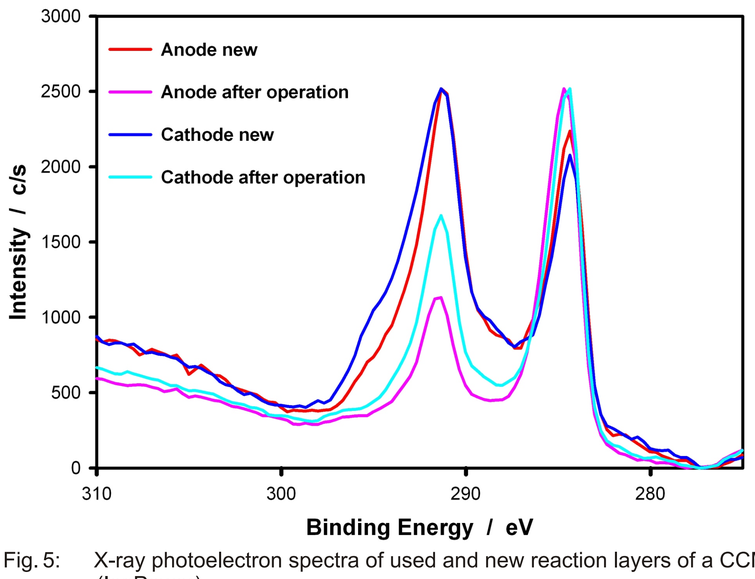

Fig. 5: X-ray photoelectron spectra of used and new reaction layers of a CCM (IonPower)

Electrochemical Characterization

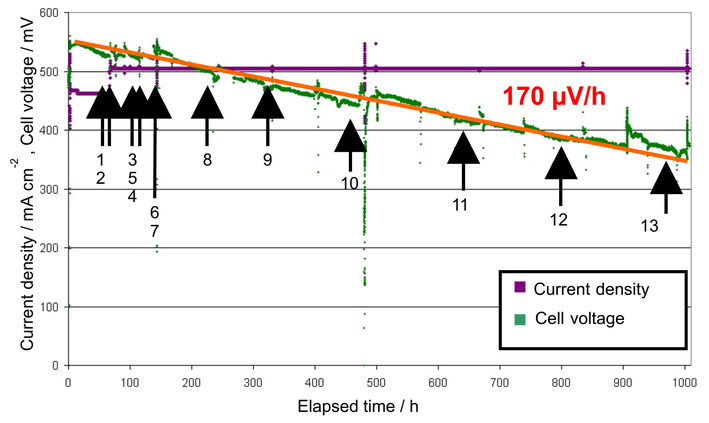

Fig. 6: Change of cell voltage during constant load at 500 mAcm^{-2} operated with H_2/air at 80°C

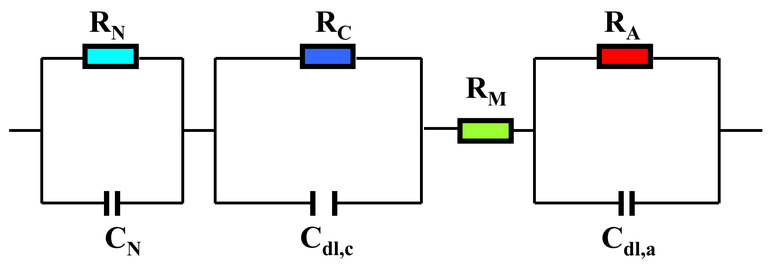

Fig 7.: Equivalent circuit for the evaluation of the electrochemical impedance measurements

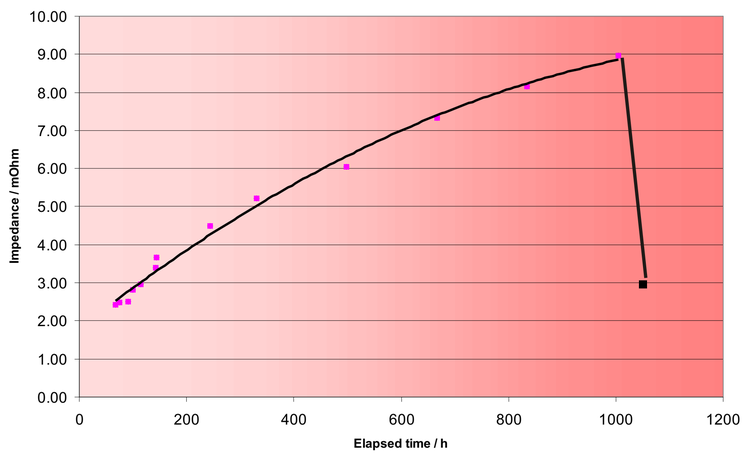

Fig. 8: Variation of the transfer resistance related to the anode reaction derived from the impedance measurement using the equivialent circuit in Fig. 2

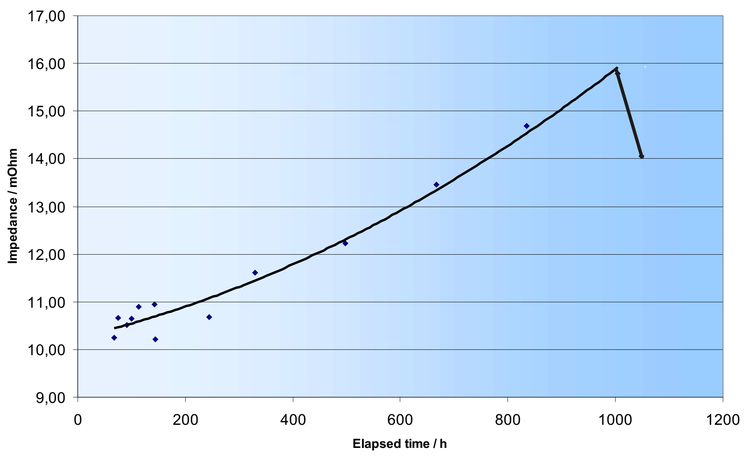

Fig. 4: Variation of the transfer resistance related to the cathode reaction derived from the impedance measurement using the equivialent circuit in Fig. 2

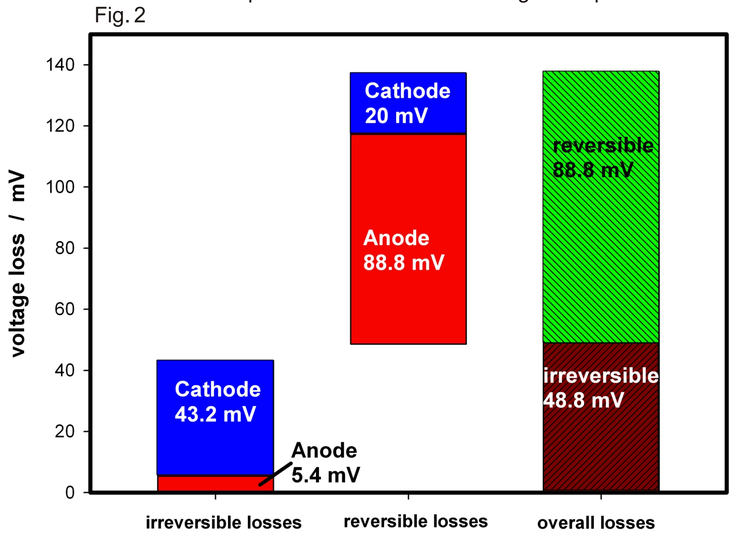

Fig. 7: Separation of the reversible and irreversible degradation individual for anode and cathode

Summary

The combined investigation of the degradation with electrochemical and physical methods allows to distinguish between reversible and irreversible degradation processes for anode and cathode individually, to identify the degradation processes, and to quantify the effect of the degradation processes to the electrochemical performance.

- Reversible and irreversible degradation can be distinguished.
- The reversible loss of the electrochemical performance is more significant than the irreversible losses in continous operation without alteration of the operation conditions.
- The degradation on the anode is mainly reversible and related to an alterated water balance.
- The degradation on the cathode is mainly irreversible and cannot be compensated by alteration of the operation conditions.
- The PTFE is partially decomposed during fuel cell operation, more significant in the anode than in the cathode, consequently the hydrophobicity decreases.
- The catalyst in the cathode agglomerates and consequently the catalyst surface area decreases.

The reversible degradation can be explained by a loss of the hydrophobicity and the irreversible degradation by the alteration of the catalysts.